Ultra-fast & Ultra-sensitive Nanostructured Hydrogen Sensors

Scientific Accomplishment

New hydrogen sensors based on palladium thin films have characteristics of being much faster, more sensitive, simpler and cheaper than any other existing hydrogen sensing system. These sensors require only monitoring of resistance, making them robust for many applications.

Hydrogen penetrates palladium metal to form palladium hydride, resulting in a 5% increase in resistance for 2% hydrogen concentrations. Thus commercial sensors that rely on monitoring the resistance of a thick palladium film in the presence of hydrogen typically suffer from low sensitivity and have a slow response time of 10 seconds to several minutes. Furthermore, commercial sensors often require heating to speed detection and get reversible behavior. In contrast to existing methods, high sensitivity to low hydrogen concentrations can be achieved by monitoring the electrical resistivity due the 11% volume change between palladium and palladium hydride within a *discontinuous* nanoscale palladium film. The swelling of the nanosized palladium grains within the film closes nanogaps within the discontinuous film, forming more conductive pathways. This results in a conductance increase of more than 50%.

The key to making discontinuous films of palladium nano-particles having a fast reversible sensing behavior lies in using a self-assembled siloxane monolayer to modify the surface tension at the palladium and glass substrate interface. Evaporation of a discontinuous nano-scale palladium film onto a bare glass substrate results in a poor hydrogen sensor because the baseline resistance is continually changing due to inconsistent movement of the palladium grains on the substrate and ultimate distortion of the conducting pathways. Application of a layer of siloxane molecules upon the glass substrate before the palladium film is deposited changes the morphology of the palladium and prevents adhesion of the palladium onto the glass surface. These film sensors consisting of 2-10 nm palladium beads have response times of about 75 milliseconds for 2% hydrogen concentrations and are capable for detecting hydrogen concentrations as low as 25ppm without elaborate signal amplification and detection.

Significance

Hydrogen is being viewed as a future energy transfer medium with intense interest because of its potential environmental benefits. As the importance of hydrogen to many industries increases, there is a greater need for high performance sensors to monitor hydrogen safety. Currently, all commercial hydrogen sensors have response times of 10 seconds or more with limited conditions for sensing hydrogen. The only other rapid sensor (with response times under 100 milliseconds) is based on electrochemically grown nanowires that rely on tedious one-at-a-time, hand fabrication methods. Our sensors represent a great advance over these nanowire based sensors. The fabrication of 2D films vs. 1D wires allows for a greater dynamic range. Furthermore, our fabrication method uses thermal evaporation of metal and application of self-assembled monolayers of siloxane which are similar to techniques used in producing integrated circuit and hence amenable to mass production.

This Argonne developed technology has received numerous inquiries from industry, is receiving additional Phase I and II funding with our industrial partner who is negotiating an exclusive license of the patent rights and this is being submitted for an R&D100 award.

Performers

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Reference

T. Xu, M.P. Zach, Z.L. Xiao, D. Rosenmann, U. Welp, W.K. Kwok, G.W. Crabtree, “Self-assembled monolayer-enhanced hydrogen sensing with ultrathin palladium films,” Applied Physics Letters **86**, Article No. 203104 (2005).

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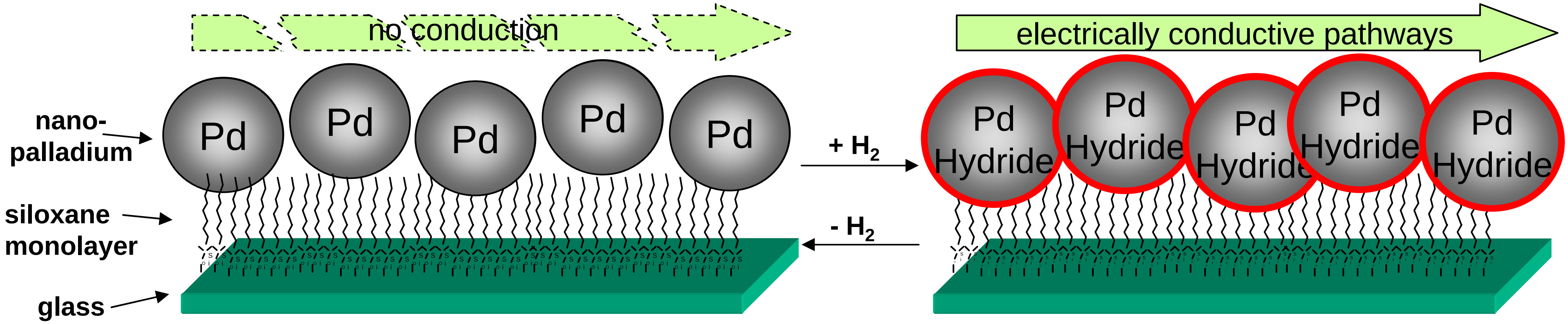
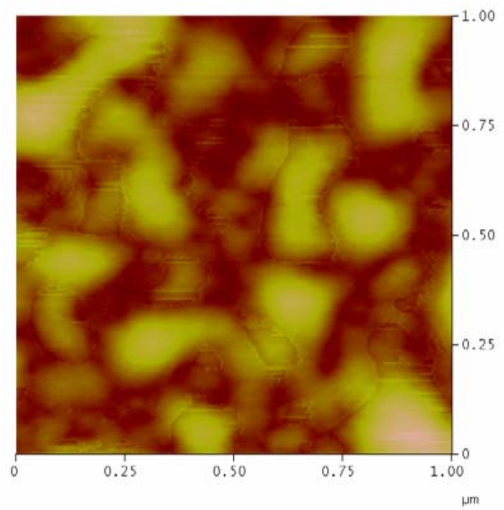
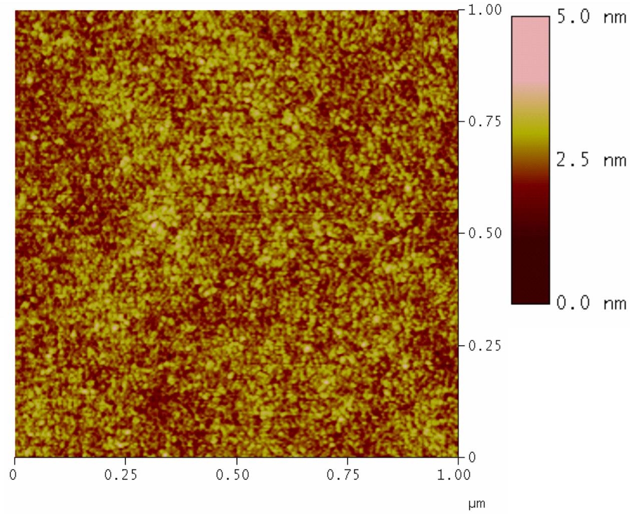


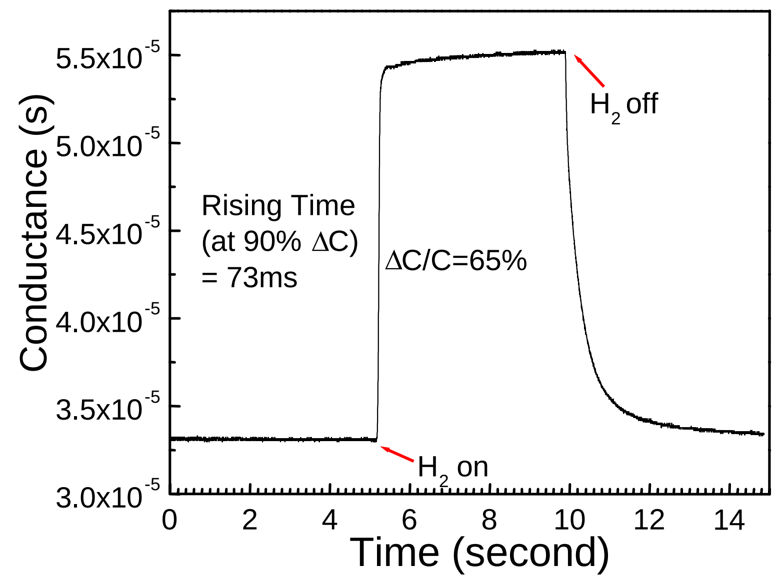
Slightly mobile nanoscale palladium nanobeads allow for detection of H_2



Palladium deposited on clean glass



Same amount of palladium deposited on siloxane coated glass



Siloxane coating on the glass modifies the morphology of the palladium film and promotes mobility of the grains. The nanosize and mobility are responsible for the rapid, completely reversible response to H_2.

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